Evidence of Network Formation in W/O Emulsion and Their Rheological Property

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(Received March 15, 2000; CL-000260)

A rheological property study on water-in-diesel oil emulsion shows the importance of network formation for the stability of the system.

It is well known that, the volume fraction, the chemical composition of the system, and the geometrical parameters of the droplets influence the rheological properties of the emulsions.[1–3] The more common emulsion formed in the petroleum industry is the water-in-oil type. In water-in-oil emulsions the strength of the interfacial film of oil that forms between the water droplets is of prime concern.[4] The stability for oil-in-water and water-in-oil emulsions is quite different. In this paper the stability and rheological properties of water-in-oil emulsions have been studied.

Water-in-diesel oil emulsions with ratio ranging from 80/20 to 10/90 have been formed with surfactant sorbitan monooleate (span 80). The contents of surfactant were always 4.67×10^{-2} mol/L exceeding the CMC to a great extent. Mixture of water and diesel oil of each sample had been performed for 10 minutes at room temperature with a shaking machine.

It has been found that in this wide range emulsions of different stability could be formed. The higher the water content, the more stable the emulsion. Figure 1 shows the state of the emulsions after one month. The W/O ratios of the samples are 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, respectively from left to right. All samples except for the last one had altered into two layers. The upper layer was a single oil phase with some small flocculates, which deposited gradually. While the bottom phase was water-in-oil type emulsion, which was proved by the immiscibility of the emulsion drops in water. Emulsion with 80% water could be stable more than one month, whereas emulsion with water content less than 10% had the shortest stability among all the samples, which altered into two phases rapidly several minutes after being formed. This fact is of great significance in practical formulation.

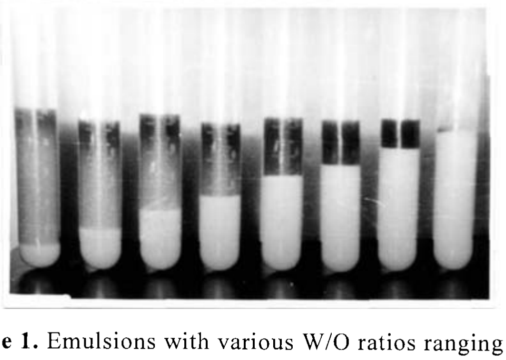

Figure 1. Emulsions with various W/O ratios ranging from 10/90 to 80/20 by volume for one month after being formed.

This phenomenon could be interpreted by the network structure formation resulted from the water droplets coagulation and coalescence. Light microscopy photographs clearly revealed the formation procession of this multi-size network (Figure 2). All photographs had been taken immediately after the completion of the emulsions with a camera installed on the light microscopy at the magnification of 400.

When W/O ratio was less than 10/90, all particles were separated (Figure 2a). There was no structure formed by particles. In the case of ratio 10/90, some particles began to aggregate forming some simple structures (Figure 2b). As W/O ratio was up to 10/90, more and more complicated structures were formed. When W/O ratio increased to 60/40, network structure formed (Figure 2c). Whereafter more complicated network structures appeared with the level of water increasing (Figures 2d and e).

Rheological property of them showed the importance of network formation for the stability of this high disperse phase content system (Figure 3). All values were determined at room temperature by a rotational cylinder viscometer made in China.

With increasing content of water in the emulsion the flow type transformed from Newtonian fluid to pseudoplastic fluid. This fact can be explained by the formation of the network structure. When the content of the water was up to 60%, network structure formation changed the rheological property of the emulsion. The viscosity of system decreased with the increasing of the shear rate, which could be attributed to the destruction of network structure when the shear rate was raised. At every increasing of the shear rate, the viscosity of the system can quickly reach a stable value within one minute. When the shear rate was changed reversely, the situation was the same and the stable viscosity value at each shear rate was nearly equal to the value when the shear rate increased. It indicated that there was no obvious hysteresis in the system and the structure could recover quickly.

From our experiment, it is clearly shown that the stability of water-in-oil emulsion is affected by the water to oil ratio. At low W/O ratio, small droplets formed, not contacting each other. As the ratio increased, droplets started coagulating and flocculating, formed not only two-dimensional but three-dimensional network. Due to the coalescence the more the water content was, the more the diversity of droplet size became, which resulted in a multi-disperse system. The lost of stability made the droplets coagulation, in turn, produced network which makes the whole system stable. Although many important papers described the forces between surfaces in liquids of different system,[5–8] the system like ours having the advantage of simplicity and intuition has not been reported. By virtue of the transparency of the system, we could get the clear microscopic picture of the interaction force, which made the droplets repulse in emulsion of low water/oil ratio and attract in emulsion of high water/oil ratio due to the short distance between the droplets.

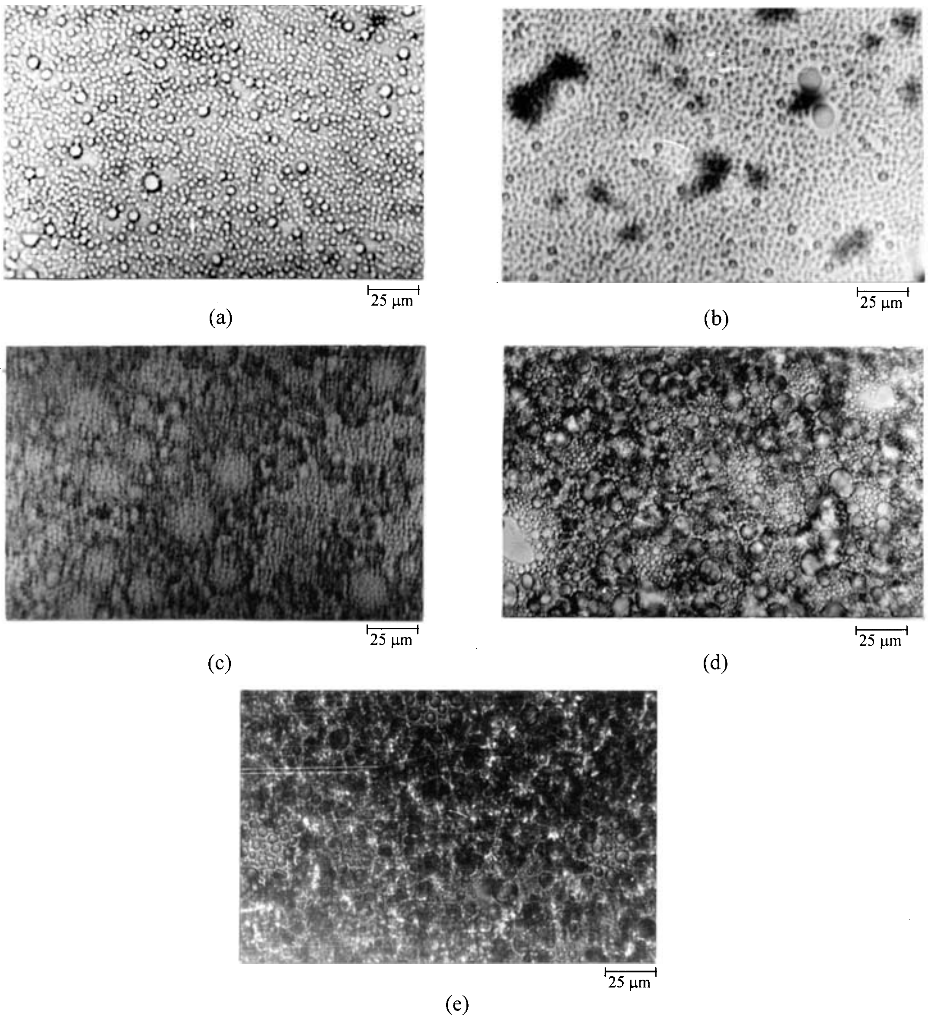

Figure 2. Light microscopy photographs of emulsions, (a) W/O<10/90. (b) W/O=10/90. (c) W/O=60/40. (d) W/O=70/30. (e) W/O=80/20.

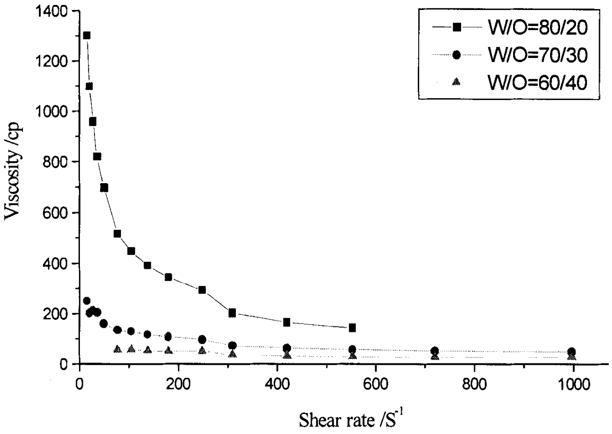

Figure 3. Rheological property of emulsions.

We gratefully acknowledge Prof. Han Da Kuang for the discussion of this paper.

References and Notes

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